4

CHEMISTRY

Syntheses and some properties of bis(furoylacetonato) metal(11) and their γ-picoline adducts

A.A. ADIMADO BSc PhD CChem MRSC

Department of Chemistry,
University of Science and Technology
Kumasi, Ghana

and

K.S. PATEL BSc MSc PhD CChem FRSC

Department of Chemistry,
University of Ibadan, Ibadan - Nigeria

ABSTRACT

The hydrated anhydrous complexes alongside the γ-picoline adducts of bis (furoylacetonato) metal(II) of the form $M(fbd)_2.nH_2O$ and $M(fbd)_2(\gamma\text{-pic})_n$, where n = 0,1 or 2, M = Mn(II), Co(II), Ni(II) Cu(II) and Zn(II):Hfbd=furoylacetone, have been prepared and characterised using microanalytical data, magnetic moment, infrared and reflectance electronic spectra. All of the complexes have octahedral geometry with the exception of $Zn(fbd)_2.H_2O$ and $Cu(fbd)_2(\gamma\text{-pic})$ which are square pyramidal. The anhydrous $Cu(fbd)_2$ is square planar.

Keywords: γ-picoline adducts, spectroscopic properties, Metal (II) furoylacetonates.

INTRODUCTION

Several uni - and bidentate nitrogeneous adducts with bis(β-diketonato) metal(II) complexes are well documented (1-9), where the bis(β-diketonato)metal (II) complexes behave as Lewis acids and form five-and six - coordinate adducts with neutral donor molecules. The stability of the adducts depends both on the basicity of the β-diketone and on that of the neutral ligand.

Though bis(furoylacetonato)M(II) (where M = Co, Ni, Cu) have been isolated (10) for the purpose of comparing the aromatic character of the furan ring with that of the chelate ring, reports of such nitrogeneous base adducts with the bis(furoylacetonato) metal(II) are unknown to the authors.

The present paper describes the synthesis and some properties of the hydrated, anhydrous and the γ-picoline adducts of bis(furoylacetonato) metal(II) of the forms; $M(fbd)_2.nH_2O$ and $M(fbd)_2(\gamma\text{-pic})_n$, where n = 0, 1 or 2; M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); Hfbd = 1-2(furyl)-1,3-butanedione; γ-pic = γ-picoline. It is of further interest to study the effect of the coordinated γ-picoline on the vibrational spectra and the electronic transitions of the parent bis(furoylacetonato) metal(II) complexes.

EXPERIMENTAL

1-(2-furyl)1,3-butanedione was purchased from Eastman Kodak Company and the metal salts were of reagent grade or purer.

The complexes $[M(fbd)_2.2H_2O]$ (M = Mn(II), Co(II), NI(II), Zn(II) and the $[M(fbd)_2]$ (M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by standard methods. (11,12) The hydrated complexes were recrystallized from 95% ethanol while the anhydrous chelates were obtained by heating the hydrates over phosphoric oxide in a vacuum pistol between 110 and 120°C. Prior to dehydration, $Ni(fbd)_2.H_2O$ and $Zn(fbd)_2.H_2O$ were obtained as monohydrates. An attempt to isolate the Fe(II) chelate starting from iron(II) ammonium sulphate, afforded a red chelate which analysed as the tris-chelate, $Fe(fbd)_3$. Infrared, UV-VIS and magnetic moment measurements gave results similar to those obtained for $Fe(fbd)_3$ in an earlier work.(13)

The adducts were obtained by an adaptation of Graddon's method.(9) This involved disolving the anhydrous $M(fbd)_2$with excess γ-picoline in petroleum ether (60-80°) and refluxing for 3-4 hours. The products were allowed to crystallize out overnight and filtered under suction. Crystals were washed with petroleum ether and allowed to dry under suction.

Microanalyses were carried out by the Microanalytical laboratory of the University of Ibadan. The analytical data for the complexes are summarized in TABLE 1.

Physical measurements. The IR spectra as KBr discs were recorded using a Perkin Elmer 283B IR spectrophotometer whilst the Diffuse reflectance spectra were recorded in the 40,000-10,000cm^{-1} range at room temperature on a Perkin Elmer UV 552 spectrophotometer equiped with a reflectance attachment, using $BaCO_3$ as reference. Peak positions were read off on a Perkin Elmer IR Data Station with a UV Programme IF 552 Disc, hooked through a Perkin Elmer 283 on-line Communication Accessory. Magnetic moment measurements were made by Gouy method.

RESULTS AND DISCUSSIONS

The analytical data given in TABLE 1 reveal monohydrates for Ni(II) and Zn(II) - furoylacetonates and dihydrates for Mn(II) and Co(II) whilst the Cu(II) chelate was obtained in the anhydrous form only. All the anhydrous bis(furoylacetonato)metal(II) complexes yielded 1:2 γ-picoline adducts except $Cu(fbd)_2$ which afforded a 1:1 adduct. Such 1:1 adducts of $Cu(acac)_2$ and $Cu(bzac)_2$ with quinoline(2) pyridine(2) and γ-picoline(2) have been reported as having magnetic moments (1,2), μ = 1.8 - 2.0B.M., which clearly established a square-pyramidal geometry for such adducts.

As a result of X-ray analysis, 5-coordination of copper(II) is established in at least seven crystalline copper(II) compounds:- copper(II) selenitedihydrate(14), tetrammine - copper(II) sulphatemonohydrate(15), anhydrous cupric formate(16) bis(dimethylglyoxime) copper(II) (16), dichloro(dimethylgloxime) copper(II)(2), di-iodo-bis(dipyridyl) copper(II)(2) and the mineral $Cu_8Mg_8(CO_3)_4(OH)_{24}.8H_2O$(17). Thus unsymmetrical 4-coordination of copper(II) is somewhat very rare.

The magnetic moments of $Cu(fbd)_2$ and $Cu(fbd)_2$(γ-pic) at 293K are 1.94 and 1.87 B.M. respectively and therefore closely resemble those(2) for $Cu(acac)_2$ and $Cu(acac)_2$(γ-pic).

The d-d absorption bands in this type of complexes are rather difficult to assign however the reflectance

ANALYSES AND

Compound	Colour	* Mpt/Decomp
$Mn(fbd)_2.2H_2O$ ($C_{16}H_{18}MnO_8$)	yellow	136-138
$Mn(fbd)_2$ ($C_{16}H_{14}MnO_6$)	brown	190-192*
$Mn(fbd)_2$(γ-pic$)_2$ ($C_{28}H_{26}MnN_2O_6$)	orange	114-116*
$Co(fbd)_2.2H_2O$ ($C_{16}H_{18}CoO_8$)	yellow	130-132
$Co(fbd)_2$ ($C_{16}H_{14}CoO_6$)	orange	> 250
$Co(fbd)_2$(γ-pic$)_2$ $C_{28}H_{26}CoN_2O_6$)	reddish	128-129*
$Ni(fbd)_2.H_2O$ ($C_{16}H_{16}NiO_7$)	leafy-green	140-141
$Ni(fbd)_2$ ($C_{16}H_{14}NiO_6$)	dark-green	177-178
$Ni(fbd)_2$(γ-pic$)_2$ ($C_{28}H_{26}H_2NiO_6$)	dirty-green	200-204*
$Cu(fbd)_2$ ($C_{16}H_{14}CuO_6$)	green	230-232
$Cu(fbd)_2$(γ-pic) ($C_{22}H_{21}CuNO_6$)	green	190-191*
$Zn(fbd)_2.H_2O$ ($C_{16}H_{16}O_7Zn$	cream	138.139
$Zn(fbd)_2$ ($C_{16}H_{14}O_6Zn$)	cream	140-142
$Zn(fbd)_2$(γ-pic$)_2$ ($C_{28}H_{26}N_2O_6Zn$)	grey	106-107*

TABLE I

MAGNETIC MOMENTS FOR THE COMPLEXES

T° C	% C		% H		% N		% Metal		μ eff.^{293K}
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	B.M.
	48.87	48.42	4.61	4.66	-	-	13.97	13.82	5.85
	53.80	53.52	3.95	4.64	-	-	15.38	15.45	5.62
	62.11	61.88	4.84	4.87	5.17	5.19	10.15	10.11	6.01
	48.38	48.10	4.57	4.62	-	-	14.84	14.36	4.96
	53.20	52.98	3.91	4.34	-	-	15.54	15.27	4.89
	61.66	61.43	4.81	5.12	5.14	5.12	10.80	10.65	5.00
	50.71	50.64	4.26	4.92	-	-	15.49	15.20	3.28
	53.24	53.24	3.91	4.15	-	-	16.26	16.26	3.13
	61.68	61.72	4.81	5.12	5.14	5.53	10.77	10.73	3.28
	52-53	52.26	3.86	4.02	-	-	17.37	17.16	1.94
	57.57	57.51	4.61	4.72	3.05	3.20	13.85	13.85	1.87
	49.83	49.58	4.18	4.98	-	-	16.95	16.79	Diamagnetic
	52.27	52.27	3.84	3.95	-	-	17.78	17.67	Diamagnetic
	60.94	60.72	4.72	4.80	5.08	5.08	11.84	11.72	Diamagnetic

TABLE II ELECTRONIC REFLECTANCE SPECTRAL DATA OF THE COMPLEXES(1kk=1000cm^{-1})

Hydrated Compd.	ν max kk	Anhydrous Compd.	ν max kk	Adduct form	ν max kk	Assignment
Mn(fbd)$_2$.2H$_2$0	37.64	Mn(fbd)$_2$	37.40	Mn(fbd)$_2$(γ-pic)$_2$	37.40	$\pi-\pi^*$(Intraligand)
	33.33		33.00		33.30	$\pi3-\pi4^*$
	28.57		28.40		28.00	$\pi-\pi^*$(Furyl)
	27.46		27.00		26.80	$^6A_{1g}(S)\xrightarrow{}{}^4T_{2g}(G)$
	21.40		21.00		20.30	$^6A_{1g}(S)\xrightarrow{}{}^4T_{1g}(G)$
Co(fbd)$_2$.2H$_2$0	37.60	Co(fbd)$_2$	37.60	Co(fbd)$_2$(γ-pic)$_2$	37.60	$\pi-\pi^*$(Intraligand)
	34.00		34.00		34.20	3^- 4^*
	32.20		32.30		32.20	
	30.03		30.00		30.05	$\pi-\pi^*$(Furyl)
	28.30		28.10		27.85	
	21.74		21.80		20.64	$^4T_{1g}(F)\xrightarrow{}{}^4T_{1g}(P)$
	19.63		19.40		19.20	
	18.52		18.10		17.75	$^4T_{1g}(F)\xrightarrow{}{}^4A_{2g}(F)$
	16.67		16.67		15.98	$^4T_{1g}(F)\xrightarrow{}{}^2E_g$
Ni(fbd)$_2$.H$_2$0	37.40	Ni(fbd)$_2$	37.20	Ni(fbd)$_2$(γ-pic)$_2$	37.40	$\pi-\pi^*$(Intraligand)
	33.90		33.20		33.86	$\pi3-\pi\ 4^*$
	28.57		28.50		28.57	$\pi-\pi^*$(Furyl)
	24.10		23.50		24.20	$^3A_{2g}(F)\xrightarrow{}{}^3T_{1g}(g)$;C.T
	21.28		21.28		20.85	
	16.39		16.00		15.75	$^3A_{2g}(F)\xrightarrow{}{}^3T_{1g}(F)$; C.T
	14.71		14.70		14.20	
	12.50		12.00		12.00	$^3A_{2g}(F)\xrightarrow{}{}^3T_{2g}(F)$
—	—	Cu(fbd)$_2$	37.40	Cu(fbd)$_2$(γ-pic)	37.50	$\pi-\pi^*$(Intraligand)
			33.60		33.60	$\pi3-\pi4^*$
			31.25		31.25	

TABLE II (contd)

			26.67		25.60	$\pi-\pi$ *(Furyl)
			21.20		21.20	C.T.
			17.54		16.66	$^2B_{1g} \longrightarrow {}^2E_g$
			15.63		15.00	$^2B_{1g} \longrightarrow {}^2B_{2g}$
			14.29		13.90	$^2B_{1g} \longrightarrow {}^2A_{1g}$
$Zn(fbd)_2 \cdot H2^0$	37.60	$Zn(fbd)_2$	37.60	$Zn(fbd)_2(\gamma\text{-pic})_2$	37.60	$\pi-\pi$ *(Intraligand)
	33.40		33.40		33.45	$\pi_3-\pi_4^*$
	29.80		29.80		29.80	$\pi-\pi$ *(Furyl)

TABLE III IMPORTANT INFRARED BANDS FOR THE COMPLEXES(cm^{-1})

Complexes	ν asyC—O	ν asyC—C—C	ν asyC—O	ν asyC—C—C	ν M-O
$Mn(fbd)_2 \cdot 2H_20$	1575(s)	1538(s)	1389(s)	1282(m)	645(s),582(s),460(w),385(m),300(m)
$Mn(fbd)_2$	1587(m)	1550(vs)	1370(vs)	1212(m)	640(s),582(s),458(m),383(w),328(m)
$Mn(fbd)_2(\gamma\text{-pic})_2$	1560(vs)	1504(vs)	1385(s)	1274(s)	620(s),560(s),448(m),363(w),313(sh)
$Co(fbd)_2 \cdot 2H_20$	1600(vs)	1575(s)	1370(s)	1250(vs)	650(s),580(m),464(w),394(m),311(m)
$Co(fbd)_2$	1595(s)	1530(m)	1315(m)	1260(m)	648(m),580(m),462(s),395(w),335(m)
$Co(fbd)_2(\gamma\text{-pic})_2$	1570(vs)	1510(vs)	1300(s)	1260(m)	633(m),568(s),450(w),385(sh),320(m)
$Ni(fbd)_2 \cdot H_20$	1592(s)	1550(vs)	1361(s)	1290(s)	660(s),579(s),465(m),402(m),314(w)
$Ni(fbd)_2$	1605(s)	1504(s)	1360(s)	1280(m)	662(s),580(m),465(m),405(w),342(sh)
$Ni(fbd)_2(\gamma\text{-pic})_2$	1600(s)	1560(s)	1330(m)	1217(w)	652(s),569(s),452(m),390(sh),330(w)
$Cu(fbd)_2$	1595(vs)	1563(s)	1399(m)	1299(m)	673(m),600(w),560(sh),556(m),350(m)
$Cu(fbd)_2(\gamma\text{-pic})$	1560(s)	1538(s)	1370(s)	1282(m)	654(s),577(m),545(sh),532(w),336(w)
$Zn(fbd)_2 \cdot H_20$	1587(s)	1554(s)	1361(s)	1285(s)	653(m),594(w),560(m),387(sh),300(w)
$Zn(fbd)_2$	1590(vs)	1570(vs)	1320(m)	1250(m)	657(s),590(w),552(w),385(w),330(sh)
$Zn(fbd)_2(\gamma\text{-pic})_2$	1570(s)	1515(m)	1370(s)	1290(s)	646(m),578(sh),530(m),375(w),315(w)

spectra of $Cu(fbd)_2$ and $Cu(fbd)_2(\gamma\text{-pic})$ (TABLE II) are found to be somewhat similar to that reported by Walker and Li(18) for related compounds.

The dihydrates $M(fbd)_2.2H_2O$ are expected to be monomeric and octahedral in geometry whilst the anhydrous $M(fbd)_2$, M=Mn(II), Co(II), Ni(II) and Zn(II) are estimated to have a polynuclear octahedral geometry like the corresponding metal(II)acetylacetonates(1). The five-coordinate monohydrate, $Zn(fbd)_2.H_2O$ is consistent with a similar square-pyramidal structure determined from X-ray study of the analogous $Zn(acac)_2.H_2O$ compound(19).

TABLE II shows the electronic transitions of the complexes. The assignments in the UV region is based on previous work(13) on the trischelates, $M(fbd)_3$. There is a general bathochromic shift of the absorption maxima in the visible region on addition of the γ-picoline. The d-d bands of the hydrates are at a higher wavenumber than those of the anhydrous forms.

The magnetic moment values given in TABLE I for the complexes are consistent with the $^6A_{1g}(S)$, $^4T_{1g}(F)$ and $^3A_{2g}(F)$ ground terms for octahedral Mn(II), Co(II) and Ni(II) ions respectively. The various other assignments made in TABLE II are consistent with those of the corresponding acetylacetonate analogues.

TABLE III summarizes some important infrared bands for the complexes. Band assignments have been made according to the literature. (1, 20-23). It does seem however that no clear correlation exists between the perturbed C-0 stretching vibrations and the strength of M-0 bonds. the bands below 700cm $^{-1}$ may be considered to contain M-0 stretching character to varying degrees because of the strong coupling between the vibrational modes of the chelate rings. It is observed from the M-0 region that adduct formation causes a low frequency shift of the M-0 stretching bands. Similar low-frequency shifts have been reported(24) for a bis(nitrogeneous base) adducts of nickel(II) acetylacetonates. This shift observed for the $M(fbd)_2(\gamma\text{-pic})_n$ adducts is probably as a result of increased electron density around the central metal ion due to inductive effect of the 4-methyl group in γ-picoline. This also confers a measure of stability on the γ-picoline adducts(9) The M-0 stretching frequencies are fairly consistent with the Irving-Williams stability order: Mn(II) > Co(II) < Ni(II) < Cu(II) > Zn(II). As a result of poor resolution in the region below 300cm $^{-1}$, it has not been possible to make any categoric M-N assignments which are expected to lie below 300 $^{-1}$ (26).

ACKNOWLEDGEMENT

The authors wish to thank Mr. Mowete for carrying out the elemental analysis. One of us (A.A.A.) wish to thank Prof. David A. Brown and Dr. Kenny Glass of the University College Dublin for allowing the use of the facilities of their laboratories.

REFERENCES

1. D.P. Graddon, "Divalent transition metal B-keto-enolate complexes as Lewis acids" CORD. Chem. Rev.4, 1 (1969)

2. D.P. Graddon and E.C. Watton, Adducts of Copper(II) B-Diketone chelates with Heterocyclic Bases". J.Inorg. Nucl. Chem., 21, 49(1961).

3. D.P. Graddon and D.G. Weeden,"Studies in the Stereochemistry of zinc(II)" Austr. J. Chem., 16 980 (1963).

4. T. Kuranchi, M. Matsui, Y.Nakamura, S. Kawaguchi and H. Kuroya, "Six Coordinated Copper(II) complexes derived from the reactions of Bis(acetylacetonato) and Bis-(ethylacetoacetato - copper(II) with some Bidentate Nitrogeneous bases", Bull. Chem. Soc (Japan) 47, 3049 (1974).

5. R.D. Gillard and G. Wilkinson, "Adducts of Bistrifluoroacetylacetonato copper(II) and the Thermochromism of Bis-B-diketonato copper(II) species", J.Chem.Soc., 5885 (1963).

6. L.L. Funck and T.R. Ortolano, "The Effect of Axial Ligation on the Ligand of Field Spectra of Copper (II) B-diketonates", Inorg.Chem.7 567 (1968)

7. J. Pradilla-Sorzano and J.P.Fackler Jr., "Base Adducts of B-ketoenolates V. Crystal and Molecular Structures of cis-Bis(1,1,1,6,6,6-

hexafluoro-2,4-pentanedionate) bis (pyridine) zinc(II) and copper(II)" Inorg.Chem. 12,1174 (1973).

8. J.P. Fackler, Jr., "The reaction of pyridine with cobalt(II) acetylacetonate in benzene. Evidence from a polymeric species". Inorg. Chem. 2 266, (1963).

9. D.P. Graddon and G.M. Mockler, Nickel(II) complexes of some O-hydroxyaryl-carbonyl compounds. II. Some substituted 2-hydroxylketones Aust. J. Chem. 21, 907 (1968)

10. T. Sasaki, K. Kanematsu and G. Kionoshita, "Synthesis of Metal Furoylacetonates and their SE Reactions. I. Studies on Heteroaromaticity X". J. Org. Chem., 33 680 (1967)

11. E.W. Berg and J.T. Truemper, "A Study of the volatile characteristics of various metal B-diketone chelates" J. Phys. Chem. 64, 487 (1960).

12. J.A. Faniran, K.S. Patel and L.O. Nelson, "Physicochemical studies of Metal B-diketonates-I Infrared Spectra of 1-(3-pyridyl)-1.3-butanedione and its divalent metal complexes" J. Inorg. Nucl. Chem. 38 77 (1976).

13. K.S. Patel and A.A. Adimado, "Physicochemical Studies of Metal B-Diketonates-VII. Spectra Studies of some Trivalent Metal complexes of 1-(2-Furyl)-1, 3-Butandedione and 4,4,4-Trifluoro-1-(2-Furyl)-1,3-Butanedione". J. Inorg. Nucl. Chem. 43, 1159(1981)

14. G. Gattow, "Structure of Cu-Selenitedihydrate at low temperature" Acta Cryst., 11 377 (1958).

15. F. Mazzi, "X-ray structure of tetraammine-copper(ii) sulphatemonohydrate". Acta Cryst., 8 137 (1955).

16. E Frasson, R. Bardi and S. Bezzi. "Structure of Cu-dimethylglyoxime at low temperature". Acta Cryst. 12 201 (1959).

17. G.D. Brunton, H. Steinfink and G.W. Beck, "Structure of the mineral $Cu_8Mg_8(CO_3)_4\ (OH)_{24}\ 8H_2O$ Acta Cryst. II, 169, (1958).

18. W.R. Walker and N.C.Li, "Metal Complexes involved in solvent Extraction and their role in the synergistic effect". J. Inorg.Nucl. Chem. 27, 411 (1965).

19. H. Montgomery and E.C. Lingafelter Crystal structure of monoaquobis (acetylacetonato) zinc. Acta Cryst. 16 748 (1963).

20. L.J. Bellamy and R.F. Branch, "The infrared spectra of chelate compounds Part (II). Metal chelate compounds of B-diketones and of salicyladehyde. J. Chem.Sos.4491 (1954).

21. B. Rao and H.B. Marthur, "Thermodynamics of Bis-Diketonato Complexes of Cu(II) and Ni(II). J.Inorg. Nucl. Chem. 33 2919 (1971).

22. G.C. Percy and D.A. Thornton, "Crystal Field Aspects of Vibrational Spectra." J.Mol. Structure, 10, 39(1971).

23. G.S. Shephard and D.A.Thornton, "Infrared Spectra of α-thenoyltrifluoroacetones of metal ions of the first transition series". Helv. Chim. Acta. 54 2212 (1971).

24. J.M. Haigh, N.P. Slabbert and D.A. Thornton, "Substituted Alkylamine Adducts of Co(II), Ni(II) and Zn(II) acetylacetonate". J. Inorg. NUcl. Chem. 32 3635 (1970).

25. H. Akaiwa, H. Kawamoto and F.Izumi, "Infrared Studies of synergistic Adducts of Bis-(2-Thenoyltrifluoroacetonate) metal(II)" J.Inorg. Nucl. Chem.37,65 (1975).

26. K. Nakamoto, C. Udovich and J.Takemoto, "Metal Isotope Effect on Metal Ligand Vibrations IV. Metal Complexes of Acetylacetone". J. Amerc. Chem. Soc. 92, 3973 (1970).